

Interactive comment on “A novel inlet system for on-line chemical analysis of semi-volatile submicron particulate matter” by P. Eichler et al.

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We thank the reviewer for his thorough review. Our specific responses are detailed below.

Reviewer: According to the authors, one of the main goals of the novel inlet is partitioning studies. These studies require a very accurate determination of instrument backgrounds in general, and the specific backgrounds in both gas and particle phase measurements. More detailed analyses of regions in the inlet and the instrument where gas phase adsorption can occur (leading to both signal losses and increased backgrounds), and analyses of background measurements which are prone to interferences from the respective other phase are needed to fully prove the usefulness of

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the inlet. Tests for quantitiveness, where instrument response (mass measured) is plotted vs particle mass introduced (e. g. varying steady state concentrations in the room) would also reveal interferences and background artifacts and should be done before publication of the inlet design.

Response: We did not state that one of the main goals of the novel inlet is partitioning studies. The obtained and shown data simply demonstrate that our set-up holds the potential for successfully carrying out such studies. This is now also more explicitly stated in the revised version of the manuscript: “Figure 5 is shown to demonstrate the potential of our novel instrumentation to study the partitioning of organic compounds between the gas and the particulate phase. Further studies are warranted to characterize potential artefacts from inlet and instrumental surfaces.” We are fully aware that SVOC partitioning measurements are difficult and prone to artefacts. Future work (including an intercomparison campaign planned for the summer of 2015) will show strengths and weaknesses of our approach. We emphasize that the scope of this manuscript is to describe a novel experimental technique and its technical implementation, to provide exemplary data on potential applications and to serve as a reference for future publications that focus on such applications.

Reviewer: Also, the authors show single mass spectra to validate their experimental setup, but they do not prove reproducibility of spectra and with that stability of their inlet system.

Response: We are not aware of any publications in the field of aerosol-MS, aerosol-CIMS or gas-phase CIMS (including PTR-MS) in which reproducibility of the mass spectra was explicitly demonstrated. Reproducibility is an implicit criterion for data being submitted for publication and our mass spectral data are indeed reproducible.

Reviewer: Not mentioned or described is the setup for “simultaneous” gas and particle phase measurements, again essential for partitioning studies. How was this done for the data shown in Fig. 5? Does the CHARON have to be removed from the PTR-MS

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to directly measure the gas phase? Is there a manifold? Again, for this switching, however it is done, a characterization of possible artifacts will be very important.

Response: We have included a Supplementary Figure S1 which shows the detailed experimental set-up for sequentially measuring the gas phase and the particulate phase. In addition we provide more details in paragraph 2.1.5: “We used different inlet configurations to measure the particulate phase of the aerosol, the instrumental background and the gas-phase component of the aerosol. The PTR-ToF-MS instrument equipped with the CHARON inlet as shown in Figure 1 (i.e. including GPD, ADL and TDU) measures the concentration and chemical composition of the particulate phase of the aerosol. The instrumental background is measured by placing a HEPA filter (HEPA-CAP 75; GE Healthcare UK Limited, Buckinghamshire, UK) upstream of the CHARON inlet. The gas-phase component of the aerosol is measured by directly sampling analyte air via a heated passivated stainless steel tube (Sulfinert, Restek, Bellefonte, USA; T=100°C, outer diameter: 6.35 mm) at a flow rate of several liters per minute. During our initial experiments this tube was capped with a submicron (0.2 μm pore size) PTFE particulate filter. To avoid any potential filter artifacts (e.g. due to off-gassing of semi-volatile compounds) we later used an inertial separator (off-axis subsampling from a high-volume flow; similar to the set-up described by Kercher et al., 2009) for particle separation. No evidence for evaporation of residual particles in the heated gas inlet was found. The gas-phase inlet is a completely independent inlet that is connected to the PTR-ToF-MS instrument immediately upstream of the drift tube via a pressure-controlled subsampling capillary made of PEEK (i.e. the standard inlet used in Ionicon PTR-MS instruments). The gas-phase inlet is zeroed by overflowing it with catalytically (Pt/Pd at 325°C) cleaned sample air. Servo motor activated valves made of passivated stainless steel (Sulfinert, Restek, Bellefonte, USA) are used for switching between different inlet configurations. The detailed experimental set-up is shown in the Supplementary Figure S1.”

Reviewer - P. 10111, I. 6-7: This statement is true in principle for all particle ionization

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techniques.

Response: The sentence has been reworded: “CI is softer but gas-particle separation remains an analytical challenge.”

Reviewer - P10112 S2.1.1.: The particle transmission efficiency in the GPD was tested for particle number losses. However, semi-volatile particle components might evaporate in the GPD, leading to particle mass losses. Measurements of particle mass (or size) after the denuder and calculations of denuder residence times and volatilization times of different semi-volatile compounds would help identify these artifacts.

Response: It is true that (partial) volatilization may occur during the 1 s period the particles reside in the GPD. Previous studies (e.g. Strommen and Kamens, 1999; Isaacman et al., 2014) have, however, shown or inferred that volatilization losses are low at such low denuder residence times. Future validation studies will certainly address this issue. We now briefly mention the potential problem:” At the given flow rate, the residence time in the denuder is only about 1 s which minimizes but does not eliminate volatilization artefacts (Strommen and Kamens. 1999). Such artefacts are not critical for the proof-of-principle data shown herein but will need to be quantified in future application studies.”

Isaacman, G., Kreisberg, N. M., Yee, L. D., Worton, D. R., Chan, A. W. H., Moss, J. A., Hering, S. V., and Goldstein, A. H.: Online derivatization for hourly measurements of gas- and particle-phase semi-volatile oxygenated organic compounds by thermal desorption aerosol gas chromatography (SV-TAG), *Atmos. Meas. Tech.*, 7, 4417-4429, doi:10.5194/amt-7-4417-2014, 2014.

Strommen, M. R., and Kamens, R. K.: Simulation of Semivolatile Organic Compound Microtransport at Different Time Scales in Airborne Diesel Soot Particles, *Environ. Sci. Technol.*, 33, 1738-1746, doi: 10.1021/es981035q, 1999.

Reviewer - P10116-10117 L26-2: A HEPA filter (also a new one) can have very high

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gas phase backgrounds itself, which would lead to an overestimation of background concentrations. I suggest testing various HEPA filters or using PTFE filters in filter holders.

Response: HEPA filters are indeed a (more or less intense) source of gas phase species. In our set-up the HEPA filter is, however, placed upstream of the entire CHARON inlet set-up, i.e. also upstream of the GPD which removes any gas-phase species emitted by the HEPA filter (see Figure S1).

Reviewer - P10117 L2-3: What kind of submicron particulate filter was used ? Were these filters tested for gas phase adsorption ? Especially quartz fiber filters are very efficient gas phase adsorbers.

Response: A PTFE filter membrane (0.2 μm pore size) filter was initially used for the experiments. We later changed to a virtual impactor set-up as commonly used for gas-phase sampling into CIMS instruments (e.g. Kercher et al., 2009). This is now detailed in the text: "During our initial experiments this tube was capped with a submicron (0.2 μm pore size) PTFE particulate filter. To avoid any potential filter artifacts (e.g. due to off-gassing of semi-volatile compounds) we later used a virtual impactor (similar to the set-up described by Kercher et al., 2009) for particle separation. To avoid any potential filter artifacts (e.g. due to off-gassing of semi-volatile compounds) we later used an inertial separator (off-axis subsampling from a high-volume flow; similar to the set-up described by Kercher et al., 2009) for particle separation. No evidence for evaporation of residual particles in the heated gas inlet was found."

Kercher, J. P., Riedel, T. P., and Thornton, J. A.: Chlorine activation by N₂O₅: simultaneous, in situ detection of ClNO₂ and N₂O₅ by chemical ionization mass spectrometry, *Atmos. Meas. Tech.*, 2, 193-204, doi:10.5194/amt-2-193-2009, 2009.

Reviewer - P10121 S3.4: This paragraph and the corresponding figure are too short to be useful as proof of concept. I suggest repeating these tests with different dilutions to show instrument response as a function of mass loading, show mass spectra

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reproducibility, and go a bit into detail in mass spectra analysis.

Response: The paragraph and the corresponding figure, even if short, are -in our opinion- useful to demonstrate that the CHARON-PTR-ToF-MS set-up can be used for the detection of organic target compounds in particles. We have reworded the paragraph to clarify why we are showing this figure and why it is an important information: "In another proof-of-principle study we used the CHARON inlet to sample 10-fold diluted cigarette smoke. Figure 6 shows the obtained PTR-ToF-MS mass scan with a prominent peak at m/z 163.12 (C₁₀H₁₄N₂⁺) corresponding to protonated nicotine. While it obviously still remains a challenge to assign the plethora of peaks in the mass spectrum to specific analytes, these data proof that the CHARON-PTR-ToF-MS set-up can be used to detect and monitor specific organic target compounds in submicron particles in real-time. It is a major advantage over existing EI-based or PI-based aerosol mass spectrometry techniques that abundant quasi-molecular ion signals, [M+H]⁺, are generated from organic target analytes. In combination with a high sensitivity PTR-QiTOF instrument (Sulzer et al., 2014), perhaps in the future even with MS-MS capability, our CHARON inlet will allow for highly sensitive and specific detection of organic target compounds in submicron particles in real time."

Reviewer - Fig. 5.: See general comments above. The figure shows that the measured gas phase signal decreases for compounds with increasing degree of oxygenation, and the authors conclude from this that "their inlet works". However, the decrease in gas phase signal could also be from adsorption of the less volatile, more oxygenated compounds in the inlet/instrument. In addition, the particle phase concentrations do not show a proportional increase – if you were to take the ratio of gas-to-particle phase it would be difficult to make a final statement on partitioning as a function of degree of oxygenation.

Response: At this stage we are only showing exemplary data to demonstrate that the CHARON-PTR-ToF-MS holds the potential of becoming a valuable tool for SVOC partitioning measurements (as acknowledged by both referees). We agree that the

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originally submitted Figure 5 is not the best way of doing this. We have produced a revised figure (given as Figure 1 below) that shows data which are closer to the obtained raw data. In combination with an improved description of the experimental set-up (see above), the revised manuscript now renders a better idea on how the data are obtained, what kind of data are obtained and what the potential future application of our set-up is. We also found an error in the background correction in the old figure. The different way of presenting the data (together with the corrected error) hopefully makes the reviewer less skeptical towards our data. We are aware of potential artefacts but the shown time series looks promising and makes us confident that “our inlet works” - or at least does not suffer from more artefacts than other MS techniques that are currently being explored for partitioning measurements. (see also reply to general comment above)

Revised text: “We also used the inlet set-up as shown in Figure S1 to measure both the particulate and the gas-phase component of the aerosol. Figure 5 shows the time traces of four selected signals: limonene (C₁₀H₁₇⁺) detected at m/z 137.13, and the three limonene oxidation products C₁₀H₁₇O₁⁺, C₁₀H₁₇O₂⁺ and C₁₀H₁₇O₃⁺ detected m/z 153.12, m/z 169.15 and m/z 185.16, respectively. The mass axis was not calibrated above m/z 137.13 which explains the relatively poor mass accuracy of the latter two signals. All signals were normalized to average signal levels detected in the gas phase (data in red). Particle-phase measurements via the CHARON inlet were conducted in the period between 16:21:00h and 16:23:40h (data in blue) after which a HEPA-filter was switched in-line upstream of the CHARON set-up (data in green). All signals decayed to background levels within 2 minutes. At 16:29:20h the gas-phase inlet was activated (data in red). To make the gas-phase signals directly comparable to the particle-phase signals, we multiplied them with an enrichment factor of 25. As expected, limonene is exclusively observed in the gas phase. A very small signal observed in the particulate phase (not visible) stems from an interfering compound at m/z 137. During instrument zeroing, the signal slowly decreased to instrumental background levels indicating that it stems from a “sticky” compound

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and not from limonene. The singly oxygenated product, C₁₀H₁₇O₁⁺, the doubly oxygenated product, C₁₀H₁₇O₂⁺, and triply oxygenated product, C₁₀H₁₇O₃⁺, show the expected increased partitioning of more and more oxygenated species into the particle phase. The higher noise in the gas-phase C₁₀H₁₇O₃⁺ signal is caused by low signal intensities which are multiplied with a factor of 25. We again refrain from going into further details or analyses. Figure 5 is shown to demonstrate the potential of our novel instrumentation to study the partitioning of organic compounds between the gas and the particulate phase. Further studies are warranted to characterize potential artefacts from inlet and instrumental surfaces.”

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/7/C4847/2015/amtd-7-C4847-2015-supplement.pdf>

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 10109, 2014.

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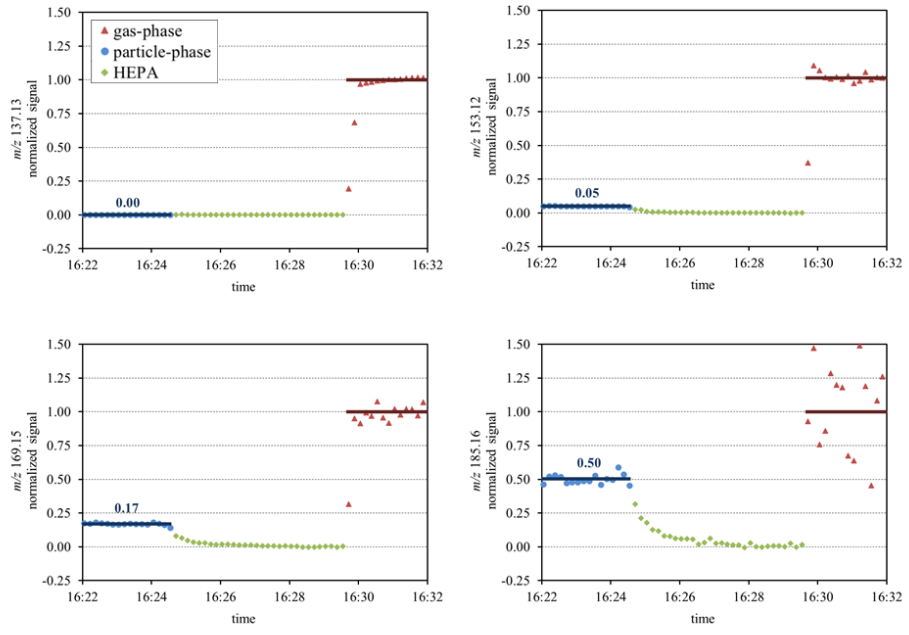


Fig. 1.

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